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THERMAL DEGRADATION OF THE OIL SHALE KEROGEN OF PULA (HUNGARY) AT 473 AND 573 K

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INTRODUCTION

The burial of the organic matter of sediments, the change of environmental parameters and mostly the increase of pressure and temperature produce the continuous transformation of the organic matter. The experiences on the processes taking place in nature, the theoretical considerations as well as the simulation experiments carried out in laboratories allowed the conclusion that the decisive parameter of the evolution of organic matter of sediments is the temperature. As to our knowledge the role of pressure is less significant.

Though the transformation is continuous, it can be divided into three phases without sharp boundaries on the basis of the nature of processes and of the type of the predominating products. The first phase, i.e. the main process of diagenesis, is an insoluble three-dimensional organic compound of complex great molecule; the formation of kerogen takes place partly by microbiological partly by chemical processes, first of all by polycondensation. The degradation of the complex molecule starts already at the end of this phase; the second phase will be the thermal degradation, i.e. the main process of katagenesis as a result of which oil and gas will be produced. During the metagenesis taking place in great depth first of all methane develops. The end-product of this evolution is anthracite or graphite.

The process is governed by the regularity that a given system tries to be in equilibrium with its environment. The system reacts to the changes of the environment with the suitable transformations. The equilibrium between the organic matter of the sediment and the enviroment is interrupted due to the burial and to the increase of pressure and temperature. The kerogen having got the new conditions is able to create an equilibrium with the new physico-chemical parameters if it will be ever more ordered, if it approximates ever more the graphite structure. Thus it is necessary that the H/C ratio should be decreased, the system should be evolved to a more coalified, more aromatic one. One of the factors of approaching the end-state (the graphite structure) is that due to the steric hindrance the cyclic components of the macromolecule, the nuclei of the units constituting the kerogen itself try to an arrangement lying parallel with the surface [TISSOT et WELTE, 1978]. Consequently, the units hindering this arrangement (aliphatic chains, hetero-atomic bonds) will be gradually eliminated. The authors above outlined the process of degradation as follows: the most sensible sites of degradation are the bonds containing hetero-atoms, especially oxygen. The carbonyl and carboxyl groups are extremely instable. Thus, during diagenesis the thermal degradation is started by the break of these

bonds. As a result of this H_2O and CO_2 are released, further smaller structural units are broken off the macromolecule which become the main components of bitumens. The greater fragments formed by this process contain mostly hetero-atoms, i.e. oxygen (resins, asphaltenes, BAM-bitumen). During katagenesis the increase of temperature results in the break of different types of bonds partly in the kerogen, partly in the bitumens produced by the preceding process. The fragments produced in this way are for the most part hydrocarbons. This phase is called by VASSOEVICH [1969] the main phase of oil formation. In the remaining kerogen the C-content and the relative quantity of the aromatic compounds is gradually increasing as it is evidenced by the elementary and IR-analyses. In the phase of metagenesis, after the release of less stable groups such a poly-condensed nucleus remains which is unable to hydrocarbon generation.

The experimental simulation of natural thermal degradation may provide assistance to discover the process of genesis, the reaction mechanism taking place in nature. Since it is impossible to simulate the long geological periods, the reaction rate is increased by the increase of temperature. The artificial "maturation" of a relatively immature kerogen under known laboratory conditions seems to be the most expedient way and then to compare it with the deeper-lying samples of a given basin. This problem has been studied by numerous researchers and many of them dealt with the thermal degradation of the oil shale kerogen. When taking into consideration the fact that the main though not only mode of industrial utilization of the oil shale is to convert the organic matter to oil during thermal treatment, this interest seems to be obvious. The usual temperature of conversion lies between 743 and 823 K, thus a group of authors studying the industrial utilization investigated the evolution process in the temperature range of 773 ± 100 K. By means of the lower temperature degradation (473 – 623 K) the type of organic matter, its gas and oil potential, the mechanism of the degradation process as well as its kinetics can be investigated. From the point of view of the industrial utilization the possibility of the in situ processes called the attention to the lower temperature degradation. This procedure may provide a more economic production than the usual retorting technique.

The major part of author believes the degradation mechanism of the oil shale kerogen to consist of two processes at least. As a first step the kerogen is transformed into bitumen and after further heating shale oil will be produced. The process is accompanied by gas generation and a part of kerogen remains in solid state. FRANKS *et al.* [1922] having registered the formation of sulfur-smelling gas and water as well of bitumen from the oil shale heated between 573 and 623 K and having observed the darkening of the oil shale, came to the conclusion that the kerogen of the oil shale consists of two types of matter. One of them is the so-called oil-producing matter from which the bitumen and with the subsequent transformation of it the oil are generated. The other type is the coal-producing matter from which the coal is developed.

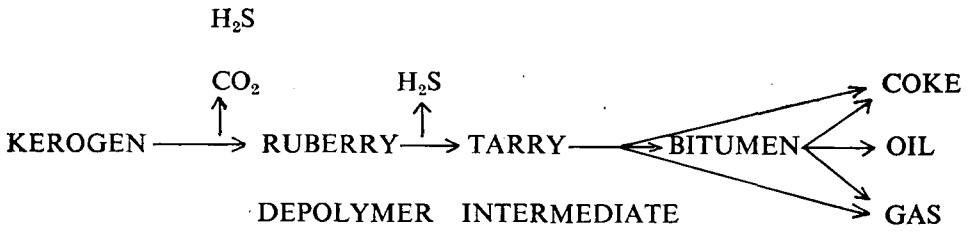
CARLSON *et al.* [1937] investigated the gases produced from the Green River oil shale during the thermal treatment between 523 and 623 K and stated that the gas formation takes place in two stages, i.e. in the initial phase due to the decomposition of kerogen, in the second phase due to the cracking of bitumen.

The main components of the gas-state products are CO_2 and CH_4 at lower temperature (i.e. around 473 K), and $C_4 - C_{12}$ hydrocarbons at higher temperatures (i.e. around 573 K). After the statement of HOERING and ABELSON [1963] the C-isotope ratio of the gas-state products developed from kerogen is similar to that of the

natural gases related to the crude oil. These observations allow to transmit the results of laboratory experiments to the natural processes.

The more particular investigation of the degradation mechanism resulted in the further refinement of the two-stage degradation. VITOROVIČ and JOVANOVIČ [1968] believe that during heating (573–673 K) the oil shale is transformed into insoluble bitumen and this process is accompanied by CO_2 and H_2O loss. Further heating produces soluble bitumen and this is accompanied by H_2S and CO_2 loss. Then the soluble bitumen is cracked to oil.

According to CANE [1951] the degradation mechanism of kerogens of algal origin is as follows:



This mechanism was experimentally evidenced by the thermal degradation of the Australian torbanite.

Most of the authors believe the process to be kinetically a first-order reaction (DIRICCO, 1956; GIRAUD *et al.*, 1970; WEITKAMP *et al.*, 1970] or a pseudo-first-order reaction [CANE, 1948, 1976] emphasizing that this is an extremely complex process the mechanism of which are insufficiently explained so far.

In this work the thermal degradation of the kerogen of the oil shale of Pula (Hungary) was investigated at 473 and 573 K in neutral gas atmosphere, heating the samples in different durations. The produced bitumen was extracted, its quantity was determined, and the detailed investigation will be neglected here. The characterization of the non-converted kerogen will be comprehended below, and the results of reaction kinetic computations will be described, respectively.

EXPERIMENTAL

Preparation of the sample

The samples to be investigated are oil shales from Hungary, formed in the Pliocene, its precursor is the *Botryococcus braunii* KÜTZ. It was formed in saline water in a crater lake of 283—285 K [JÁMBOR and SOLTI, 1976]. The air-dry sample was ground to the grain size of 0.05—0.15 mm. The moisture, ash, CO_2 and organic carbon contents were determined (see Table 1). The soluble organic matter was extracted in Soxhlet extractor by means of chloroform (BIT-A), then by the mixture of benzene—acetone—methanol of 75:15:15 ratio (BAM-bitumen). Kerogen was separated from the inorganic components by differences in specific gravity, i.e. by physical accumulation. Table 1 shows the degree of purity (ash content, CO_2) of the kerogen as well as the data characteristic of the organic matter content (C_{org}). Though the ash content of kerogen is rather high, i.e. 9 percent, it has been believed that it would be more expedient to investigate a less pure concentrate which has undergone no chemical effect during the isolation procedure since this will provide the possibility to make comparison with the more diagenized samples of the basin.

TABLE 1

Some organic and inorganic data of the oil shale and kerogen

	Oil shale	Kerogen
Ash %	49,9	9,0
CO_2 %	9,5	2,2
C_{inorg} %	2,6	0,6
Bit-A %	3,3	—
BAM %	1,3	—
C_{org} %	27,4	70,2

Thermal degradation method

5—10 g of the kerogen prepared in the afore-mentioned way was weighted into glass-boat and was put into ignition glass tube. The heating of the ignition tube was carried out in a furnace equipped with programmed heating. The system was thoroughly washed with nitrogen at room temperature, then it was heated at 473±5 resp. 573±5 K during one, seven and fourteen days under continuous nitrogen flow. The gas-state products were not retained. Fluids (water, and occasionally oil) were condensed in air-cooled trap. The sample was cooled to room temperature also under nitrogen flow. The solid rest was extracted in the mixture of benzene:acetone:methanol in Soxhlet equipment in order to determine the H/C ratio and quantity of the bitumen formed during degradation. The solid matter remained after extraction (unconverted kerogen) was dried at 333 K.

The effect of thermal treatment on the unconverted kerogen has been characterized by the H/C ratio, by the volatile material ratio and by the C_R/C_T ratio.

The determination of the hydrogen and carbon contents was carried out in CHN-1 analysator.

The volatile material ratio equals to the material loss at 773 K heated during 30 minutes in inert atmosphere referring to unit carbon, according to the ASTM Standard (Standard Methods of Laboratory Sampling and Analysis of Coal and Coke D271—48 in 1952, Book of ASTM Standard, 1952).

The C_R/C_T ratio was adapted by GRANSCH and EISMA [1966] from coal chemistry to characterize the organic matter of the sediments. The value of the quotient is determined by the type and diagenesis degree of the organic matter. If one of these factors is the same in all samples to be compared, the deviation of the quotient is caused only by the other parameter. Adapting the procedure applied in coal chemistry, the samples were pyrolized at 1173 K during 90 minutes under nitrogen atmosphere and the carbon content of the original material (C_T) and of the thermally treated sample (C_R) was measured. The kerogen investigated by us is immature and is far of the coalified state, consequently, the treatment at lower temperature seemed to be suitable to its characterization. The oil shale samples were heated at 573, 773, 873 and 1173 K and the C_R/C_T ratio was determined at each temperature. It has been found that thermal treatment ought to be carried out at 773 K (or maximum at 873 K) in order to compare the samples of the same degree of diagenesis from the point of view of comparison of the organic matter contents [HETÉNYI *et al.*, 1977]. In the present measurements we started from a given kerogen concentrate which has been artificially "matured" during the experiments. Thus, the type of the organic matter is the same and from the quotient conclusions can be drawn to the degree of diagenesis. To choose the temperature 773 K is verified also by the

fact that in the low temperature thermal degradation (423—623 K) of the Green River oil shale kerogen taken as basis for comparison CUMMINS *et al.*, [1974] used to characterize the unconverted kerogen the "carbon residue ratio". This represents the amount of carbon residue formed at 773 K per unit of organic carbon.

Results

The conversion of the organic matter of oil shale into oil takes place at about 743—823 K under industrial conditions. The process of degradation, however, starts at much lower temperature. Nevertheless, depending on the temperature applied and on the duration of degradation the composition of products will change and the structure of the unconverted kerogen will more or less change as compared to the original untreated kerogen. In our laboratory experiments considerable quantity of gas has developed from the organic matter degraded at 473 and 573 K during one, seven and fourteen days, since the first moments of the thermal treatment. Small quantity of water, resp., at 573 K small quantity of oil also developed which were condensed already to the effect of air-cooling in the flask fitted to the outlet of the ignition tube. The colour of kerogen deepened from the original ochre-yellow: first it became lighter than darker brown. The gases were not analyzed, in order to obtain information these were transported through a tube filled with soda-asbest. From fading it has been registered that relatively great amounts of CO_2 were developed. The gas formation can be followed since the start of the process, the gas quantity has perceptibly decreased in the course of the process.

The quantity of water and oil is very small. The pH-value of water proved to acid in general (i.e. 3 to 5). At 473 K no oil formation was observed. At 573 K slight oil film developed during one day, during seven, resp., fourteen days a drop of dark-brown oil of high H/C ratio (1.91) was formed. On the basis of the IR-spectra of the oil, it contains long-chain oxygen-bearing compounds.

After the thermal treatment the solid phase was extracted again. Since during preparation the originally present soluble organic matter was removed, the repeated

TABLE 2

Quantity and composition of BAM-bitumen

Heating time (days)	BAM-bitumen			
	Quantity %	C %	H %	Atomic H/C ratio
0 (Original oil shale)	1,3	70,2	10,3	1,76
		473 °K		
1	2,5	74,6	10,9	1,75
7	0,8	62,8	8,7	1,69
14	0,7	67,9	9,6	1,69
		573 °K		
1	1,9	—	—	—
7	0,8	69,7	9,7	1,67
14	0,8	76,5	10,6	1,66

extraction produced the thermally developed bitumen. The quantity of the so-called BAM-bitumen formed during the thermal degradation of kerogen at 473 and 573 K and being soluble in the mixture of benzene:acetone:methanol of 75:15:15 ratio can be seen in Table 2 in percentage of the starting kerogen. The quantity of bitumen formed during degradation is remarkable: after one-day treatment 2.5 percent at 473 K resp. 1.9 percent at 573 K. Our paper does not aim the particular investigation of the formed soluble organic matter, the quantities of the BAM-bitumen was determined only in order to characterize the quantitative relations of the converted and unconverted organic matter, resp., to study the reaction mechanism itself. In first approximation this fraction was characterized by the atomic H/C ratio. According to the data of Table 2 considerable change follows in the quantitative relationships of the bitumen fractions after one and seven days. After the thermal treatment of seven and fourteen days only 30—40 percent of the bitumen produced during one day remains, the other part is degraded. It is worthy of mention that after the seven-day treatment and under the applied experimental conditions the quantity of the extractable BAM-bitumen remains constant independently of the time and temperature, i.e. about 0.8%. At the same time, the atomic H/C ratio proves to be relatively the same both at 473 and 573 K and both during seven and fourteen days, i.e. 1.69 resp. 1.66—1.67.

The atomic H/C ratio of the extracted bitumen is 1.75 after the treatment at 473 K and during one day, i.e. it shows the same value as the original oil shale (1.76). Though the decrease of the H/C value is rather slight, when taking this into account together with the quantitative relations this may lead to the conclusion that at the given temperature the part of the primary bitumen formed from kerogen was further degraded as a secondary process. Also during the degradation of the bitumen the components rich in hydrogen were first removed, thus the remaining soluble organic matter becomes somewhat more "coalified".

It seems so that under the applied experimental conditions the equilibrium follows in this phase of degradation during seven days; the bitumen production is presumably continued and at the same time the formed bitumen is degraded again.

TABLE 3

Properties relating differences in the kerogen of the heated residues

Heating time (days)	C %	H %	Atomic H/C ratio	Volatile material ratio	C_R/C_T
0	70,2	10,3	1,76	128	0,07
			473 °C		
1	71,3	10,0	1,68	115	0,11
7	73,1	9,6	1,58	106	0,14
14	69,4	9,0	1,55	107	0,21
			573 °K		
1	70,7	9,7	1,65	106	0,20
7	71,1	9,1	1,53	100	0,23
14	72,6	8,8	1,45	87	0,28

The decrease of the perceptible gas products in this phase as well as the facts above relate to the formation of other types of compounds during the secondary degradation of the formed bitumen, and to the restricted measure of bitumen formation and degradation as compared to the first phase of the process, respectively.

The unconverted kerogen remained after the removal of the soluble thermal fraction has been characterized by its H/C ratio, volatile content and C_R/C_T ratio. These data are in close relationship with the structure of the kerogen. The H/C ratio expresses the number of H-atoms per C-atoms, i.e. it is the measure of the saturation of the system. The volatile material ratio, i.e. the quantity of the components mobilized at 773 K (gas, water, oil) referring to the unity organic carbon, may reflect the state of condensation of the system. If kerogen is built up by strongly condensed cyclic structures, small quantity of volatile material will be released. In our case the C_R/C_T ratio, or the degradation factor [GIRAUD, 1974] shows the degree of diagenesis. The carbon and hydrogen contents, the H/C ratios, the volatile material ratio as well as the degradation factor of the original kerogen and of the unconverted kerogen degraded at 473 and 573 K during one, seven and fourteen days are comprehended in Table 3.

The degradation factor of the studied original kerogen is very low (0.07). The organic matter is immature and is of high H/C ratio (1.76). According to other gradual degradation experiments proceeded by $KMnO_4$ it was produced mostly by straight-chain fatty acids and is a highly polymerized organic macromolecule, the proportion of the aromatic constituents can be neglected.

In the course of the simulation experiments by means of which only the effect of time and temperature tried to be investigated disregarding the other factors, the degradation factor is definitely growing. At both temperatures the value shows slight rise between one and seven days, between seven and fourteen days the rise is steeper *(Fig. 1)*. The two curves are nearly parallel with each other, i.e. at 473 K

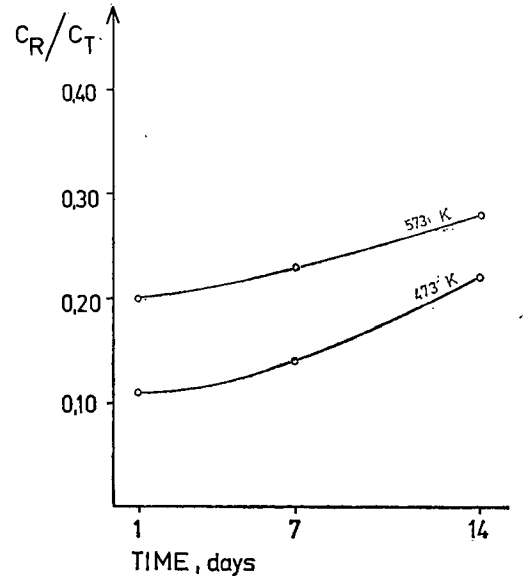


Fig. 1. Change of the C_R/C_T ratio during the heating period

the time dependence of the C_R/C_T value is similar. As a function of the duration of thermal treatment the H/C ratio shows slight decrease *(Fig. 2)*. The change is somewhat more expressed at 573 than at 473 K.

Regarding the absolute values of the two quotients, of the degradation factor as well as of the atomic H/C ratio, a relatively immature kerogen remains after the simulation experiments. On the basis of these quotients the thermally treated organic matter can be qualified also as alginite kerogen. The H/C and at 1173 K the C_R/C_T values are 1.4—1.8 resp. 0.09—0.27 in case of the alginite kerogen [GRANSCH and EISMA, 1966]. The same values of the unconverted kerogen comprehended in Table 3

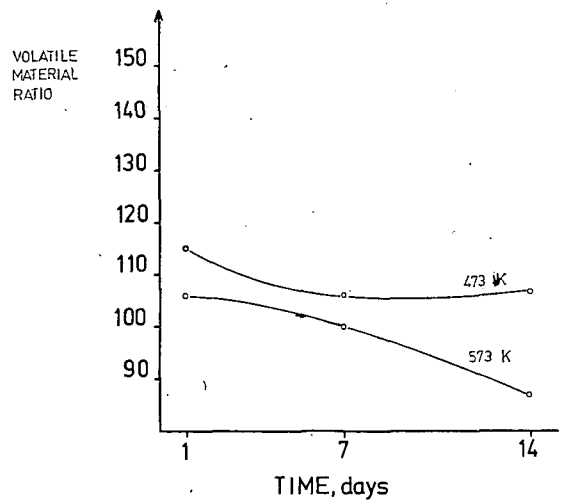


Fig. 2. Change of the volatile material ratio during the heating period

are within the given limits, especially when taking into consideration the lower temperature at which the degree of degradation was measured (773 K). During this relatively short low-temperature degradation process the oil shale kerogen of Pula did not reach the state of the humic coals where the C_R/C_T (measured at 1173 K), resp., the H/C ratio would be 0.60—1.00 resp. 1.4—0.4. To reach these values higher temperature is needed. At 573 K the increase of duration would produce, further degradation. During the thermal degradation carried out with the Green River oil shale the change of the H/C ratio is similar: at 473 K after 90-days thermal treatment 1.31, after 360 days 1.21. At 573 K this value decreased from 1.38 to 1.25 during 0.5 and 4.0 days [CUMMINS *et al.*, 1974].

The proportion of the volatile material decreases between one and seven days at 473 K *(Fig. 3)* and remains unchanged between seven and fourteen days. At the same time, at 573 K the whole process shows a decreasing tendency, moreover between seven and fourteen days this tendency becomes more expressed. Apparently, at 473 K the measure of condensation of the sample hardly changes as a function of time. The less stable groups are released already at the beginning of thermal treatment in form of gas and occasionally of small quantity of water. Equilibrium follows in the bitumen formation. The decrase of the quantity of the unconverted material is continuous. The further degrading part of the forming bitumen is released also in form of gas. The measure of degradation is slight, thus the measure of conden-

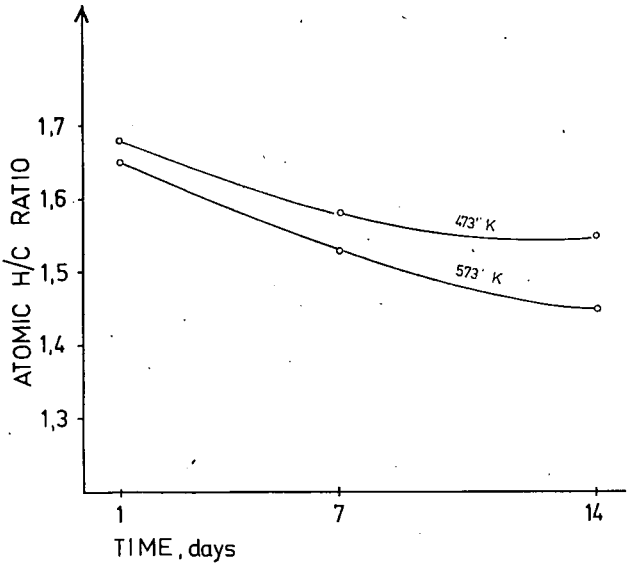


Fig. 3. Change of the atomic H/C ratio during the heating period

sation of the unconverted kerogen hardly differs from that of the original kerogen. At 573 K the degradation becomes more expressed, after seven days small quantity of oil has also developed. Both the formation and the further transformation of the bitumen increased. The oil consists of long-chain compounds which derive from the kerogen itself through the bitumen. By means of the break of longer-chain peripheric units the kerogen becomes relatively more condensed, thus the proportion of the volatile material decreased. These experiences are in harmony with the measurements of CUMMINS *et al.* [1974] mentioned above, i.e. the proportion of volatile material of the Green River oil shale degraded at 473 K is relatively constant as a function of the duration of degradation and at 573 K definite decrease can be observed. In case of the oil shale kerogen of Pula the volatile material is less in its proportion at 473 K but definite decrease has been measured. This deviation can also be attributed to the less mature state of the oil shale of Pula.

The thermal degradation of oil shale kerogens proceeding at lower temperatures is a reaction consisting of numerous complex part-processes. Regarding kinetically the whole of the process the reaction is first-order [DIRICCO, 1956; HUBBARD and ROBINSON, 1950; CUMMINS and ROBINSON, 1972], or pseudo-first-order, at least [CANE, 1976].

Consequently, the temporal change of kerogen concentration is as follows:

$$-\frac{dc}{dt} = kt$$

When taking the starting quantity of organic matter as unit, and when the quantity of degraded kerogen is x at any t time, the quantity of the unconverted kerogen will

be: $1-x$. Integrating the equation above and substituting these values, the equation of a straight line will be obtained:

$$-k = \frac{2.303 \log (1-x)}{t}$$

When plotting $\log (1-x)$ as a function of time, a straight line ought to be obtained if the reaction is a first-order one. The specific reaction rate, "k", can be computed from the rise of the straight line.

In Table 4 the quantity of the converted kerogen degraded at 473 and 573 K during one, seven and fourteen days, that of the unconverted kerogen $(1-x)$ as well as the logarithm of the latter are demonstrated. When plotting these values *(Fig. 4)* a straight line has been obtained at both temperatures. The rise of these lines were determined and the k-values were computed. At 473 K $k=5.31 \cdot 10^{-2}$/day; at 573 K $k=8.86 \cdot 10^{-1}$/day. As a result of a temperature increase of 100 K the specific reaction rate has increased by about 17-times.

TABLE 4

Quantity of the converted and unconverted organic matter and the specific reaction rate

SAMPLE	Temperature (K)	Time (days)	x	$1-x$	$\log (1-x)$	k (per days)
OIL SHALE	473	1	0.076	0.924	−0.0343	$3.18 \cdot 10^{-1}$
		14	0.114	0.886	−0.0526	
KEROGEN	473	1	0.027	0.973	−0.0119	
		7	0.030	0.970	−0.0132	$5.31 \cdot 10^{-2}$
		14	0.033	0.967	−0.0146	
	573	1	0.122	0.878	−0.0565	
		7	0.170	0.830	−0.0799	$8.86 \cdot 10^{-1}$
		14	0.217	0.783	−0.1059	

When comparing the values determined in this way with those computed by CUMMINS and ROBINSON [1972], i.e. at 473 K $k=2.4 \cdot 10^{-4}$/day and at 573 K $k=2.9 \cdot 10^{-2}$/day, it can be seen that the specific reaction rate of the kerogen investigated by us is greater at both temperatures. Especially great difference is found at lower temperature. This can be explained by the fact that the oil shale kerogen of Pula is rather immature as evidenced also by the measurements, thus a lot of groups of weaker bonds is connected to the matrix which break off rapidly at relatively low temperature. The process was accompanied by intense gas formation, very small quantity of water was observed, resp., considerable quantity of bitumen was formed. When increasing the temperature the stronger bonds could also be affected by the thermal degradation, consequently taking the k-values at 573 K of the kerogens of Pula and of Green River the differences are smaller.

At this temperature the kerogen is degraded into bitumen but during the sequent degradation not only water and gas develop, but small quantity of oil co-subuld also be observed.

By means of the thermal degradation experiments the conversion the insoluble organic matter itself, i.e. of the kerogen had to be investigated, thus it was separated from the inorganic components. The measurements of CUMMINS and ROBINSON

[1972] were carried out on oil shale and not on kerogen. The presence of the inorganic components has presumably effect on degradation, i. e. it may change the rate of it. Consequently, the comparison of the values concerning the Green River oil shale and the kerogen analyzed by us is not exact. To support our assumption the oil shale of Pula has also been thermally degraded at 473 K, i.e. at the temperature where

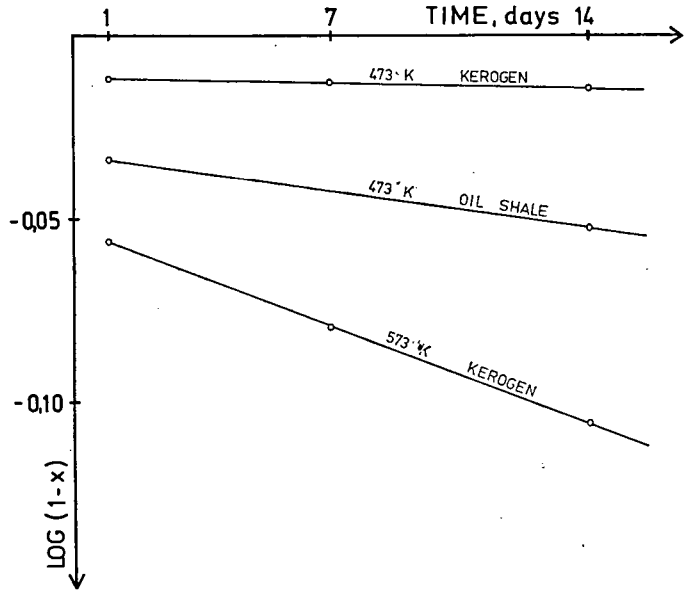


Fig. 4. First-order plot for 473 and 573 K data

the greater difference has been observed in the k-values. The $\log(1-x)$ — time relation is plotted in *Fig. 4,* then having determined the rise of the curve the k-value was computed: $k=3.18 \cdot 10^{-1}$/day. As a result of the effect of inorganic components the specific reaction rate increased by more than one order of magnitude.

SUMMARY

The thermal degradation of the oil shale kerogen of Pula (Hungary) was investigated at 473 and 573 K during one, seven and fourteen days in neutral gas atmosphere. The degradation mechanism, the structural changes of the unconverted kerogen were investigated as well as kinetic computations were carried out.

The organic matter of the original oil shale is a complex macromolecule formed from algal fatty acids, the proportion of its aromatic components is low.

In the course of thermal degradation considerable quantity of bitumen developed, the further decomposition of which produced gas-state compounds at 473 K and small quantity of oil at 573 K. The quantity of the extractable bitumen is independent of time and temperature after seven days, of course under the given experimental conditions. Equilibrium follows in the formation and decomposition. The atomic H/C ratio, i.e. the type of bitumen shows considerable differences after one day, after the thermal treatment of seven, resp., fourteen days it is practically the same.

As a result of thermal treatment first the least stable groups, the short-chain units are broken off, this is manifested in the intense gas formation since the start of the reaction. This is followed by the degradation of the longer-chain peripheric compounds: the main phase of formation of the bitumen fraction. After one day the role of secondary processes increases as a function of time until the formation and degradation of bitumen get the equilibrium. In the course of the secondary degradation also the hydrogen-rich components are first eliminated, the atomic H/C ratio decreases, but this "coalification" is of very small measure.

The formation of gas, water and oil takes place directly from the kerogen or through the bitumen state. Simultaneously, structural changes are taking place in the kerogen molecule which result in the increase of its condensed state and coalification.

On the basis of the atomic H/C ratio and of the degradation factor the original kerogen is immature, and after maturation followed during the thermal treatment and measured by the parameters above it does not reach the state of humic coals and lignites, either. The character and measure of change are similar to those measured in the simulation experiments of the Green River oil shale. The difference showing in the values of quotients can be attributed to the less mature state of the oil shale kerogen of Pula. For the same reason, the proportion of the volatile material at 473 K does not depend on the duration of thermal treatment of the Green River oil shale, while in case of the kerogen of Pula the increase of duration of thermal treatment is accompanied by slight but definite decrease of this proportion. It is assumed that the less stable groups of the immature kerogen are able to gradual elimination already at this relatively low temperature while in case of more mature oil shale the degradation follows only at higher temperature (573 K). The thermal energy of 573 K is suitable to activate the structural units in respect of which no considerable difference exists between the two materials. Thus, at this temperature the volatile material ratio decreases in both samples as a function time, i.e. the sample became more condensed.

From the kinetic point of view the thermal degradation is a first-order reaction. The specific reaction rate is $5.31 \cdot 10^{-2}$/day at 473 K. As a result of the temperature increase of 100 K this value increases by about 17-times, i.e. at 573 K it is $8.81 \cdot 10^{-1}$/day. Both values are higher than the corresponding values of the Green River oil shale. As it has been demonstrated by the data concerning the structural characteristics of the unconverted kerogen (H/C, C_R/C_T, proportion of volatile material) the thermal behaviour of the two samples differs first of all at low temperature (473 K) just due to the structural features. This difference is shown also in the results of the kinetic computations, especially when the kerogen of the oil shale Pula is not isolated but the oil shale itself is degraded. In this case, presumably due to the catalytic effect of the inorganic components the reaction rate increases, the specific reaction rate will be $3.18 \cdot 10^{-1}$/day at 473 K.

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REFERENCES

CANE, R. F. [1948]: The chemistry of the pyrolysis of torbanite. Journal et Proceedings, p. 62—68.
CANE, R. F. [1951]: The mechanism of the pyrolysis of torbanite. — In: Oil shale and cannel coal, 2, Institute of Petroleum, London.

CANE, R. F. [1976]: The origin and formation of oil shales. — In: Oil shale, edited by T. F. YEN and G. V. CHILINGARIAN. Elsevier Scientific Publishing Company, p. 27—61.
CARLSON, A. J. [1937]: Inorganic environment in kerogen transformation. — In: W. E. ROBINSON of Mines Research, 7968, p. 40.
CUMMINS, J. J., F. G. DOOLITTLE and W. E. ROBINSON [1974]: Thermal degradation of Green River kerogen at 150° to 350 °C. Composition of products. BuMines RI 7924, p. 18.
CUMMINS, J. J. and W. E. ROBINSON [1972]: Thermal degradation of Green River kerogen at 150° to 350 °C. Rate of product formation. BuMines RI 7620, p. 15.
DIRICCO, L. and P. L. BARRICK [1956]: Pyrolysis of oil shale. Industrial and Engineering Chemistry, Vol. **48**, No. 8, p. 1316—1319.
FRANKS, A. J. and B. D. GOODIER [1922]: Preliminary study of the organic matter of Colorado oil shales — In: W. E. ROBINSON and K. E. STANFIELD: Constitution of oilshale kerogen: Bibliography and Notes on Bureau of Mines Research, 7968, p. 39—40.
GIRAUD, A. [1970]: Application of pyrolysis and gas chromatography to geochemical characterization of kerogen in sedimentary rock. AAPG Bulletin **54**, No. 3, p. 439—455.
GRANSCH, S. A. and E. EISMA [1966]: Characterization of the insoluble organic matter of sediments by pyrolysis — In: Advances in Organic Geochemistry, edited by G. D. HOBSON and G. C. SPEERS, p. 407—427, Pergamon Press.
HETÉNYI, M., K. MAITZ and É. TÓTH [1977]: Contributions to the knowledge of the Hungarian oil shale kerogen I. Preliminary report on the results of the pyrolysis and selective oxidation. Acta Miner. Petr., **XXIII/1**, p. 165—175.
HOERING, T. C. and P. H. ABELSON [1963]: Annual report of the director of the Geophysical' Laboratory, 1962—1963, Carnegie Inst. Wash. Year Book, **62**, p. 229—234.
HUBBARD, A. B. and W. E. ROBINSON [1950]: A thermal decomposition study of Colorado oil shale. BuMines Rept. of Inv. 4744, p. 24.
JÁMBOR, Á. and G. SOLTI [1976]: Geological conditions of the Upper Pannonian oil shale deposit recovered in the Balaton Highland and at Kemeneshát (Transdanubia, Hungary) — Annual Report of the Hungarian Geological Institute of 1974. p. 193—220.
TISSOT, B. P. and D. H. WELTE [1978]: From kerogen to petroleum — In: B. P. TISSOT and D. H. WELTE: Petroleum formations and occurrence, Springer-Verlag, p. 148—184.
VITOROVIČ, D. K. and L. J. JOVANOVIČ [1968]: Solubility of Aleksinac oil shale kerogen III. Solubility of preheated kerogen. Glasnik Hemijskog Drustva, Vol. **33**, No. 8—9—10, p. 581—588.
WEITKAMP, A. W. and L. C. GUTHERLET [1970]: Application of a microretort to problems in shale pyrolysis. Ind. and Eng. Chem., Process Design. Development, v. **9**, No. 3, p. 386—395.

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